

EP  
302 289

Code: 243-6003

EUROPEAN PATENT OFFICE  
EUROPEAN PATENT NO. 302,289 A1

Int. Cl.<sup>4</sup>: C 08 K 5/20  
C 08 K 5/16  
C 08 K 5/32  
C 08 L 57/08  
C 09 D 3/64  
C 09 D 7/12  
//(C 08 L 67/08  
67:24)

Application No.: 83111516.6

Filing Date: July 18, 1988

Date of Publication  
of the Application: February 8, 1989  
Bulletin 89/06

Priority:  
Date: August 5, 1987  
Country: AT  
No.: 1976/87

Designated Contracting States: BE, CH, DE, ES, FR, GB,  
IT, LI, NL, SE

PROCESS FOR REDUCING FORMALDEHYDE EMISSIONS WITH ACID CURING  
LACQUERS BASED ON ALKYD RESIN-UREA RESIN COMBINATIONS

Applicant: Vianova Kunstharz AG  
Box 191, Leechgasse 21  
A-8011 Graz, AT

Inventors: Edmund Urbano  
Grazer Strasse 34  
A-8045 Graz, AT

Andreas Illaazewicz  
Koschatgasse 17  
A-8020 Graz, AT

Elisabeth Ospelt  
Unterhal 412  
A-8051 Graz, AT

The present invention concerns a process for reducing the free formaldehyde content and formaldehyde emissions with acid curing lacquers based on alkyd resin-urea resin combinations. C-H acid compounds which contain an acidic alpha-methylene group and a nitrogen in an amide linkage are added as substances. Additives of 0.2 to 10 wt% (based on the solid substance of the alkyd resin-urea resin combination) of the compounds claimed according to this invention, preferably cyanoacetamide or acetoacetamide (each in 30% solution in ethanol) definitely reduce the free formaldehyde content and formaldehyde emissions without causing turbidity or reduced shelf-life of the lacquer or forming craters and a loss of gloss in the lacquer film.

The present invention concerns a process for reducing the free formaldehyde content and formaldehyde emissions with acid curing lacquers based on alkyd resin-urea resin combinations.

Acid curing alkyd resin-urea resin combinations are used on a large scale for lacquering wood, e.g., for furniture or for sealing parquet floors. Their advantages include rapid drying and the good mechanical and chemical stability of the applied lacquer films.

An important disadvantage of this class of binders is the odor problem to which the processor is exposed due to the emission of formaldehyde from the wet lacquer film. Formaldehyde is manifested by a pungent odor even in low concentrations (about

8 ppm) and is also highly toxic (MAC value (maximum allowed job site concentration): 1 ppm = 1.2 mg/m<sup>3</sup> air).

Numerous proposals for eliminating this problem are known from the literature.

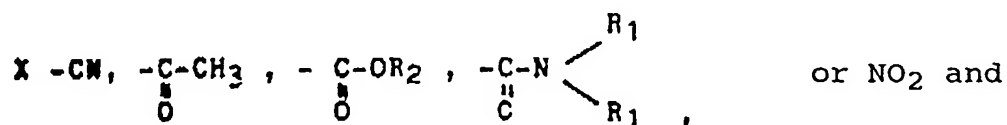
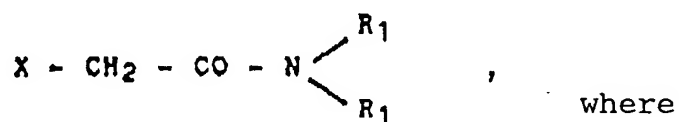
For example, there have been attempts to reduce the free formaldehyde content by adding substances to bind formaldehyde such as ammonia, amines and their salts (Czechoslovakian Patent 195,006), hydrazine derivatives (Japanese Kokai Patent 49/105,558), urea, thiourea and ethyleneurea (Japanese Kokai Patent 49/42,737, Austrian Patent 367,445, German Patent OLS 3,143,969), acrylamide polymers (U.S. Patent 4,346,181), ketones,  $\beta$ -diketones and  $\beta$ -keto acid esters (French Patent 2,575,754, Polish Patent 72,885, European Patent 2,596, Japanese Kokai Patent 48/85,741), Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (Czechoslovakian Patent 185,020) and sulfur compounds (U.S. Patent 4,264,760).

In most cases these measures do not have any negative effects because the free formaldehyde content can be reduced only temporarily and is rapidly increased again to the original level. Furthermore, practical experience has shown that even resins with a very low free formaldehyde content develop strong formaldehyde emissions during the film-forming reaction.

Addition of "formaldehyde scavengers" is appropriate only when a substantial reduction in odor burden during the hardening of the lacquers is achieved in this way. Furthermore, the added substances must be effective even in small quantities proportionally for economic reasons, and they must also be sufficiently compatible with alkyd resin-urea resin combinations in order to prevent turbidity or reduce shelf life of the lacquers as well as disturbances in the lacquer film such as formation of craters or loss of gloss.

It has now been found that formaldehyde emissions in processing alkyd resin-urea resin combinations can be reduced greatly by adding C-H acid compounds which have an acidic alpha-methylene group and a nitrogen in an amide linkage in the molecule.

The present invention thus concerns a process for reducing the free formaldehyde content and formaldehyde emissions by acid curing lacquers based on alkyd resin-urea resin combinations, characterized in that 0.2 to 10 wt%, preferably 0.3 to 5.0 wt%, based on the solid substance of the alkyd resin-urea resin combination, of a compound that has an acidic alpha-methylene group with a pKa value (at 25°C in water) of 0.5 to 14.0, preferably 8.0 to 13.5, and a nitrogen in an amide linkage in the molecule is added according to the general formula



$R_1$  is a hydrogen atom or an alkyl group with 1 to 18 carbons and  $R_2$  is an alkyl group with 1 to 18 carbons.

These compounds as such as well as in the form of their C- methylol compounds and optionally N-methylol compounds such as those obtained in the reaction with free formaldehyde are readily soluble in the resin combinations and also have no negative effects on the lacquer or the lacquer coatings produced from them within the claimed limits.

The preferred formaldehyde binding substances are cyanoacetamide, acetoacetamide and their N-mono- or -dialkyl

derivatives such as those obtained by reaction of the corresponding esters with primary amines, e.g., with fatty amines.

The compounds are added before/during/after production of the acid curing alkyd resin-urea resin combination, preferably in the form of a 30 wt% solution in ethanol, ethylene glycol, N-methylpyrrolidone, water or some other solvent suitable for the lacquer system. The compounds of the urea resin components are preferably added.

The composition of acid curing lacquers based on alkyd resin-urea resin combinations as well as the synthesis of the components for such combinations are well known to persons skilled in the field.

In the following example an alkyd resin-urea resin combination which is defined as follows is used:

Acid curing, plasticized urea resin for production of single-component and two-component lacquers for industrial surface finishing of wood and wooden materials. How supplied: 60% in ethanol/butanol; viscosity: 220-320 s (DIN 53,211/20°C); acid value (as delivered): less than 8 mg KOH/g (DIN 53,402), consisting of 44 parts short-oil, air-drying alkyd resin with 82% solid resin. Oil content: 39%. Acid value 5-15 mg KOH/g (DIN 53,402), viscosity 150-200 s (70% in ethanol, DIN 53,402), 38 parts urea resin with 62% solid resin, acid value less than 2 mg KOH/g (DIN 53,402) and a viscosity of 60-150 s as delivered (ethanol, DIN 53,211/20°C) and 28 parts butanol.

A lacquer based on the resin combination given above with the following composition was tested:

### Lacquer A

- a) 92 parts by weight resin (60%) = (55.2 parts solid resin)  
4 parts by weight xylene  
2 parts by weight ethyl glycol acetate  
2 parts by weight butyl acetate  
100
- b) 10 parts by weight p-toluenesulfonic acid solution (10% in ethanol)

### Lacquer B

2 wt% cyanoacetamide (based on solid resin of the alkyd resin-urea resin combination) as a 30% solution in ethanol was added to lacquer component A a.

### Lacquer C

2 wt% acetoacetamide (based on solid resin of the alkyd resin-urea resin combination) as a 30% solution in ethanol was added to lacquer component A a.

### Lacquer D

2 wt% cyanoacetamide (based on solid resin of the alkyd resin-urea resin combination) was added as a 30% solution in ethanol to the urea resin before being combined with the alkyd resin and then after adding the alkyd resin the batch was mixed well for 1 hour at 60°C.

## Reference lacquer E

2 wt% cyclohexane-1,3-dione (based on solid resin of the alkyd resin-urea resin combination) was added as a 30% solution in ethanol to lacquer component A a.

The free formaldehyde in the lacquer was determined according to the sulfite method according to DIN 53,187 yielding the following values:

	Lacquer				
	A	B	C	D	E
Free formaldehyde wt% based on lacquer					
After storage for 1 day	1.0	0.4	0.5	0.3	0.8
After storage for 3 months	1.2	0.4	0.5	0.35	0.8

The formaldehyde emissions were determined according to the following method: The lacquer to be tested was applied by means of a paint applicator to a weighed glass plate with a wet film thickness of 300  $\mu\text{m}$  and the glass plate was immediately placed in a closed glass container with the dimensions 22 x 12 x 6 cm through which 80 mL/min air was flowing. This air was passed through a 0.1% solution of 2-hydrazono-2,3-dihydro-3-methylbenzothiazole hydrochloride in a recipient. The formaldehyde content was determined photometrically after adding 10% iron(III) chloride solution. This method is described in detail in Handbook of Photometric Analysis of Organic Compounds by B. Kakac and Z. Vejdelek, Verlag Chemie. A time-dependent quantity diagram is obtained on the basis of several measurements. The measurement cycle was concluded after 24 hours. Then the quantity of lacquer was determined by

reweighing. This quantity is used as a reference point for preparing the emission curve. (For results see Table I.)

Table I

Zeit <sup>①</sup>	② Summe der Formaldehydemissionen *)				
③ Stunden	④ Lack A	⑤ Lack B	⑥ Lack C	⑦ Lack D	⑧ Lack E
0.5	0.16	0.06	0.09	0.05	0.12
1.0	0.47	0.14	0.18	0.12	0.34
1.5	0.64	0.21	0.25	0.18	0.48
2.0	0.76	0.28	0.32	0.24	0.63
2.5	0.87	0.34	0.37	0.28	0.78
3.0	1.00	0.39	0.45	0.32	0.95
5.0	1.65	0.67	0.79	0.52	1.56
7.0	2.16	0.97	1.32	0.78	2.09
24.0	3.00	1.53	1.74	1.29	2.97

\* mg/g dry film

Key: 1 = Time  
 2 = Total formaldehyde emissions\*  
 3 = Hours  
 4 = Lacquer A  
 5 = Lacquer B  
 6 = Lacquer C  
 7 = Lacquer D  
 8 = Lacquer E

The technical lacquer properties were not affected by the additives (for results see Table II).

The lacquers were tested by the following methods:

(1) Measuring the drying time on a drying recorder, wet film thickness about 150  $\mu\text{m}$ , running time 6 hours; a/b/c

a = running time

b = surface drying

c = complete drying

Results given in minutes.



(2) Measured according to DIN 53,157 at 120 and 300  $\mu\text{m}$  wet film thickness, results given in minutes.

(3) Hours at 26°C until incipient gelation

Table II

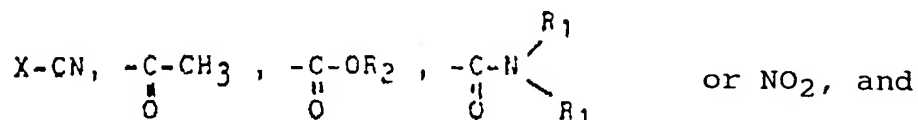
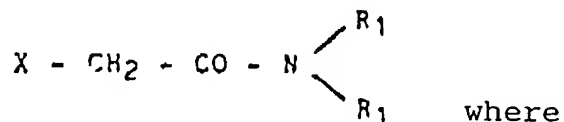
① Prüfung	② Methode	③ Lack A	④ Lack B	⑤ Lack C	⑥ Lack D
⑦ Trocknung	(1)	8 13 17	9 13 27	10 15 20	8 13 19
⑧ Pendelhärte	(2)				
⑨ nach 3 h		26 92	23 89	22 77	29 83
⑩ nach 6 h		84 137	164 109	58 120	70 135
⑪ nach 24 h		141 194	128 172	135 169	140 168
⑫ Potlzeit	(3)	51	50	50	60

Key: 1 = Test  
 2 = Method  
 3 = Lacquer A  
 4 = Lacquer B  
 5 = Lacquer C  
 6 = Lacquer D  
 7 = Drying  
 8 = Pendulum hardness  
 9 = After 3 hours  
 10 = After 6 hours  
 11 = After 24 hours  
 12 = Pot time

### Claims

1. Process for reducing the free formaldehyde content and formaldehyde emissions with acid curing lacquers based on alkyd resin-urea resin combinations, characterized in that 0.2 to 10 wt%, preferably 0.3 to 5.0 wt%, based on solid substance of the alkyd resin-urea resin combination of a compound which has an

acidic alpha-methylene group with a pKa value (at 25°C in water) of 0.5 to 14.0, preferably 8.0 to 13.5, and a nitrogen atom in an amide linkage in the molecule is added, corresponding to the general formula



$R_1$  is a hydrogen atom or an alkyl group with 1 to 18 carbons and  $R_2$  is an alkyl group with 1 to 18 carbons.

2. Process according to Claim 1, characterized in that cyanoacetamide, acetoacetamide or their N-alkyl derivatives are used as the added compound.

3. Process according to Claims 1 and 2, characterized in that the compound is used in the form of a 10 to 50 wt% solution in ethanol, ethylene glycol, N-methylpyrrolidone, water or some other solvent suitable for the resin system.

4. Process according to Claims 1 to 3, characterized in that the compound is added to the urea resin component.



European  
Patent Office

EUROPEAN SEARCH REPORT

EP 88 11 1516

RELEVANT DOCUMENTS			Classification of the application
Category	Characterization of the document, citing the relevant sections, if necessary	Concerns Claim No.	
A	US-A-3 917 558 (J.J. GARDIKES et al.) * Claims *	1	C 08 K 5/20 C 08 K 5/16 C 08 K 5/32 C 08 L 67/08 C 09 D 3/64 C 09 D 7/12 // (C 08 L 67/08 C 08 L 61:24 )
A	EP-A-0 155 194 (MITSUBISHI PETROCHEMICAL CO. LTD.) * Claims, page 9, line 6 to page 10, line 13 *	1	
A	EP-A-0 138 448 (THE WIGGINS TEAPE GROUP LTD.) * Claims *	1	Specialized fields where search was conducted
A	DE-A-1 282 952 (VEB LEUNA-WERKE "WALTER ULBRICH") * Claim *	1	C 08 K C 08 L C 09 D
			Categories of documents cited
			X: of special importance A: technological background O: unwritten publication P: intermediate literature T: theories or principles on which the invention is based E: conflicting application D: document cited in the application L: document cited for other reasons
<input checked="" type="checkbox"/> The present search report was compiled for all patent claims.			&: member of the same patent family, corresponding document
Location of search THE HAGUE		Concluding date of search NOVEMBER 11, 1988	Examiner DE LOS ARCOS Y VELAZQUEZ